J. Chem. Thermodynamics 42 (2010) 1126–1130

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Relation between the characteristic molecular volume and hydrophobicity of nonpolar molecules

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ARTICLE INFO

Article history:
Received 19 November 2009
Received in revised form 31 March 2010
Accepted 16 April 2010
Available online 22 April 2010

Keywords:
Hydrophobicity
Hydration
Aqueous solutions

ABSTRACT

Experimental values of the Gibbs free energies of hydration for a set of nonpolar or very slightly polar compounds are analyzed in order to investigate how does the hydrophobic effect depend on molecular structure and shape. The contribution due to the hydrophobic effect is evaluated using a method we suggested previously. A number of values of the Gibbs free energies of solvation in dimethyl sulfoxide and in hexadecane, which are required for calculation, were determined by gas chromatographic headspace analysis. It is found that the Gibbs hydrophobic effect energy is linearly dependent on characteristic molecular volume for a large variety of solutes with branched and unbranched carbon chains, different functional groups and atomic composition. Molecular structure and shape do not significantly affect the hydrophobicity of chemical species, and molecular volume is a main factor determining it.

1. Introduction

The hydrophobic effect is being intensively studied using both theoretical and experimental methods [1–3]. One of the important questions is how the structure of a molecule relates to its hydrophobicity.

Thermodynamic functions of hydration of solute A $\Delta_{hyd}f^{A}$ ($f = G, H, S$) are greatly influenced by the hydrophobic effect. Their experimental values are a good starting point to analyze this phenomenon using various models of hydration. Alternatively, one can study hydration of idealized objects such as hard particles in computer simulations. The energy of hydration of a hard particle is the cavitation energy of water. Using Monte-Carlo methods [4] and information theory approaches [5], it was shown that the Gibbs free energy of hydration of relatively small hard spherical particles is proportional to the volume of a particle (for molarity-based standard states). The study of hydration of non-spherical hard particles with different shape [6] also showed that the Gibbs free energy of hydration is primarily governed only by the volume of a particle.

Real solutes behave very differently from hard particles. A plot of the Gibbs free energies of hydration *versus* molecular or molar volumes of real solutes cannot be approximated by a single curve [7]: different classes of nonpolar solutes (*e.g.* alkanes, arenes, and noble gases) lie on different straight lines with different slopes and intercepts. This is because real solutes engage in different degrees of intermolecular interactions with water. For solutes without the ability of hydrogen-bonding or donor–acceptor bonding, these interactions are called nonspecific interactions. Their energy is dependent on solute structure.

The question of whether and how intermolecular interactions influence the hydrophobicity of real molecules has not been answered. It is necessary to analyze the values of $\Delta_{hyd}f^{A}$ using some extrathermodynamic model in order to distinguish the effects caused by the hydrophobic effect from those caused by nonspecific interactions. In the present work, we report a thermodynamic analysis of experimental Gibbs free energies of hydration for a number of nonpolar compounds to investigate how does the hydrophobic effect depends on molecular structure and shape.

2. Methodology

Recently, we suggested [8] that a dramatic difference between magnitudes of the Gibbs free energy of hydration of nonpolar solutes and their Gibbs free energy of solvation in 'regular' solvents can be expressed in terms of the Gibbs energy of the hydrophobic effect, $\Delta_{h.e.}G^{A}$. The Gibbs free energy of hydration can be considered as the sum of the Gibbs energy of the hydrophobic effect and the Gibbs nonspecific hydration energy, $\Delta_{hydr(nonsp)}G^{A}$. Here and below the energies are at $T = 298$ K; the molar fraction scale of concentration is used and the standard pressure is 1 bar. The last quantity can be calculated using a general empiric equation for the Gibbs nonspecific solvation energy, which has been shown [9] to be correct for various non-associated solvents. This equation is given by:

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doi:10.1016/j.jct.2010.04.011